



Preparation of carbon-coated Magneli phases Ti_nO_{2n-1} and their photocatalytic activity under visible light

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ABSTRACT

Carbon-coated Magneli phases Ti_nO_{2n-1} were prepared by a simple heat treatment of the powder mixture of rutile-type TiO_2 with poly(vinyl alcohol) PVA at 1100 °C in inert atmosphere. The lower TiO_2 /PVA ratio in the mixture resulted in Ti_nO_{2n-1} with the lower n -value. Carbon-coated Ti_nO_{2n-1} phases thus prepared showed photocatalytic activity under visible light. The Ti_nO_{2n-1} phases with n -values of 2 and 3 had higher activity under visible light than those with n -values of more than 4. Carbon coated on the particles was found to reduce the matrix rutile-type TiO_2 to Magneli phases Ti_nO_{2n-1} during the heat treatment, in addition to suppress the sintering and grain growth of Ti_nO_{2n-1} particles and to enhance the photocatalytic activity by increasing local concentration of the pollutant due to its adsorptivity.

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1. Introduction

The development of photocatalyst anatase-type TiO_2 was considered to be one of the promising processes for environment conservation and remediation [1–5]. Numerous works have been performed from various points of view. Urgent demand on the conservation of global environment and its protection from pollution promoted strongly the research works on photocatalysis. We have been working on the development of carbon-coated TiO_2 to hybridize photocatalytic activity with adsorptivity and getting certain success [6–13]. On carbon-coating process, the formation of reduced phase of TiO_2 , which has been called Magneli phase and expressed as Ti_nO_{2n-1} , was observed [6,14,15].

Since ultraviolet rays, which can activate anatase-type TiO_2 photocatalyst, is contained only less than 4% in solar light, the development of visible light active photocatalyst is strongly demanded. Various visible light active photocatalysts have been proposed; TiO_2 doped by different anions, carbon [16–21], sulfur [22,23] and nitrogen [24–27], and TiO_2 doped by different cations, such as Cr and V [28], and C^{4+} and S^{4+} [29]. In these TiO_2 doped by either anion or cation, some lattice defects, possibly oxygen vacancies, are reasonably supposed to be associated with these dopants

in disordered arrangement. Magneli phases of Ti_nO_{2n-1} , which were prepared by the interaction of anatase-type TiO_2 with coated carbon, showed also activity under visible light [14,15]. These Magneli phases were known to be formed by the introduction of oxygen vacancies into rutile-type structure in ordered arrangement [30,31]. One of reduced phases of WO_3 , $W_{18}O_{49}$, in which oxygen vacancies located in WO_3 lattice in ordered arrangement, was shown to have appreciable photoactivity under visible light [32,33]. Therefore, the presence of lattice defects, possibly oxygen vacancies, in either ordered or disordered manner, seems to be an important factor to form visible light sensitive photocatalysts. From this point of view, the formation of Ti_nO_{2n-1} by a simple process, i.e., heat treatment of the powder mixture of TiO_2 and carbon precursor, is interesting for practical applications of the photocatalyst.

In the present work, Magneli phases Ti_nO_{2n-1} with different n -values were successfully synthesized from rutile phase TiO_2 by heat treatment of its mixture with poly(vinyl alcohol), resulting in carbon-coated Ti_nO_{2n-1} , and their photoactivity under visible light was studied.

2. Experimental

2.1. Preparation of carbon-coated Ti_nO_{2n-1}

Rutile-type TiO_2 , which was a commercially available (TTO-55(N), Ishihara Sangyo Co., Ltd.), was mixed with poly(vinyl alcohol)

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PVA (Reagent grade, Wako Co., Ltd.) in powder with different mass ratios. The pristine TiO_2 consists of a single phase of rutile structure of the primary particle with the size of about 10 nm, few of which were aggregated to form the secondary particles. PVA used has the particle size of about 1–2 μm and the average polymerization degree of about 3500.

The powder mixture with a mixing ratio TiO_2/PVA of 50/50 was heat-treated at different temperatures from 700 to 1100 °C for 1 h in a flow of N_2 gas with a flowing rate of 50 mL/min (sample code TP50-700–TP50-1100). During the heat treatment, trace amount of oxygen in N_2 gas was excluded by using pure Ti metal as a getter. Heating rate to the programmed temperature was 5 °C/min. The powder mixtures with different mixing ratios of TiO_2/PVA from 95/5 to 20/80 were heat-treated at 1100 °C for 1 h under the same conditions as above (sample code TP95-1100–TP20-1100). For the comparison, the original TiO_2 (TP100) was also heat-treated at 700 °C for 1 h (TP100-700). The heat treatment conditions are listed in Table 1.

2.2. Characterization of carbon-coated $\text{Ti}_n\text{O}_{2n-1}$

Crystalline phases of titanium oxide formed after the heat treatment were identified from X-ray powder diffraction pattern using Cu K α radiation by referring to JCPDS cards. BET surface area was determined from adsorption isotherm of N_2 at 77 K. Particle morphology was observed under scanning electron microscope with acceleration voltage of electron beam of 5 kV.

Photocatalytic activity of the sample powders was evaluated from the decomposition rate of iminocadine triacetate IT ($\text{C}_{24}\text{H}_{53}\text{N}_7\text{O}_6$) and phenol Ph ($\text{C}_6\text{H}_5\text{OH}$) in an aqueous solution with a concentration of 0.62×10^{-4} and 5.4×10^{-4} mol/dm³, respectively. The sample powder of 0.1 g was dispersed by stirring in the 100 dm³ solution under the irradiation of fluorescent light, in which the components with the wavelength of less than 400 nm (*i.e.*, UV rays) were cut off by using a filter. Color-fastness equipment with 15 fluorescent lamps (40 W \times 15) was used for irradiation. The change in the concentration *c* of IT and Ph remained in the solution was measured from the absorbance at 205 and 269 nm, respectively, in absorption spectra of high-performance liquid chromatography (HPLC) on the sampled solution by referring to the respective calibration curve determined in advance. The decomposition rate *k* was determined from the slope of the plot of the concentration in solution relative to initial concentration, *c/c*₀, in logarithmic scale against irradiation time, which could be approximated to be linear. In advance of photoactivity measurement, the sample powder was

kept in either IT or Ph solution for 200 h in the dark at room temperature, in order to get saturation of the adsorption of each pollutant.

Diffuse reflectance spectrum was measured on the sample powders using a spectrometer with a reflectance mode in a wavelength range of 250–700 nm.

3. Results

3.1. Formation of $\text{Ti}_n\text{O}_{2n-1}$ phases

The original rutile-type TiO_2 (TP100) was white fine powder. After the heat treatment at 700 °C without mixing of PVA (TP100-700), the powder looked to become coarse than before, but was white. After the heat treatment with PVA at a temperature above 700 °C, however, the powders became black in color, even the sample prepared with the smallest amount of PVA, TP95-1100. Even after carbon coating, the samples were still powdery, so that any pulverization was not needed for further characterization.

In Fig. 1a, change in XRD pattern with heat treatment temperature is shown for the mixture with $\text{TiO}_2/\text{PVA} = 50/50$.

Even after the heat treatment up to 800 °C, no change in XRD pattern was detected, showing sharp diffraction peaks, which could be indexed by rutile structure. Above 900 °C, rutile phase was partially reduced probably to Ti_4O_7 , and the original rutile phase remained up to 1000 °C. At 1100 °C, however, rutile phase disappeared completely and a single phase of one of Magneli phases, Ti_4O_7 , was formed. All the diffraction peaks observed on 1100 °C-treated sample (TP50-1100) could be indexed by Ti_4O_7 structure. On this series of samples, no diffraction peak for carbon was observed, even though PVA was already carbonized and all samples after the heat treatment looked black, revealing that the formed carbon had amorphous structure.

This experimental result shows that rutile-phase TiO_2 can be reacted with carbon produced from PVA to form Magneli phase. In order to complete reduction by this process, however, it is necessary to heat up to 1100 °C.

In Fig. 1b, XRD patterns after the heat treatment at 1100 °C are shown for the mixtures with different TiO_2/PVA ratios. Crystalline phases identified from XRD pattern are listed in Table 1.

In the samples prepared from the mixtures with TiO_2/PVA of more than 90/10 (samples TP95-1100 and TP90-1100), a part of the original rutile-phase TiO_2 remained as unreacted. The Magneli phases formed in these samples are identified to be Ti_9O_{17} . In the sample prepared from the TiO_2/PVA ratio of 80/20, TP80-1100, Ti_6O_{11} and Ti_5O_9 , are

Table 1
Preparation condition and characteristics for carbon-coated $\text{Ti}_n\text{O}_{2n-1}$ phases prepared from rutile-type TiO_2 .

Sample code	TiO_2/PVA	Heat treatment condition	Crystalline phase	BET surface area (m ² /g)	Rate constant <i>k</i> ($\times 10^{-4}$ h ⁻¹)	
					For IT	For Ph
TP100	100/0	–	Rutile	39	–	–
TP100-700		700 °C, 1 h	Rutile	2	–	–
TP50-700	50/50	700 °C, 1 h	Rutile			
TP50-800		800 °C, 1 h	Rutile + Ti_4O_7			
TP50-900		900 °C, 1 h	Ti_4O_7 + rutile			
TP50-1000		1000 °C, 1 h	Ti_4O_7 + rutile			
TP50-1100		1100 °C, 1 h	Ti_4O_7			
TP95-1100	95/5	1100 °C, 1 h	Rutile + Ti_9O_{17}	–	–	–
TP90-1100	90/10		Ti_9O_{17} + rutile	1	1.3	1.7
TP80-1100	80/20		Ti_5O_9 + Ti_6O_{11}	1	0.5	3.7
TP60-1100	60/40		Ti_4O_7 + Ti_3O_5	4	1.4	–
TP50-1100	50/50		Ti_4O_7	21	1.8	5.3
TP40-1100	40/60		Ti_2O_3 + Ti_3O_5	38	5.4	–
TP30-1100	30/70		Ti_2O_3 + Ti_3O_5	44	8.0	–
TP20-1100	20/80		Ti_2O_3 + Ti_3O_5	45	9.4	7.0

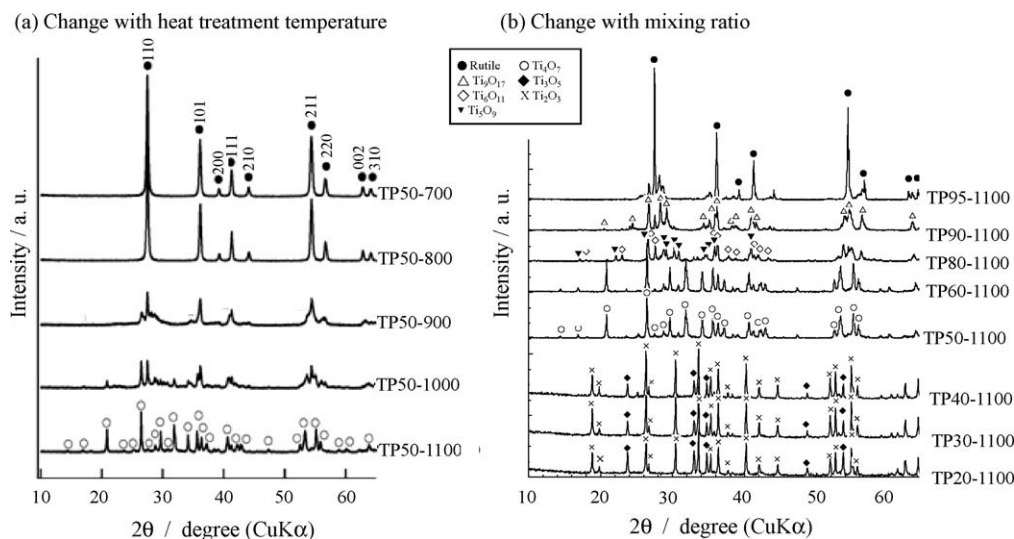


Fig. 1. Changes in X-ray diffraction pattern with (a) heat treatment temperature and (b) mass ratio of TiO_2/PVA .

formed, no rutile-type TiO_2 being detected. In the samples from TiO_2/PVA ratios of 60/40 and 50/50, TP60-1100 and TP50-1100, the principal Magneli phase is Ti_4O_7 , particularly the latter seeming to be a single phase. In the samples from TiO_2/PVA ratios of 40/60, 30/70 and 20/80, TP40-1100, TP30-1100 and TP20-1100, two phases Ti_3O_4 and Ti_2O_3 co-exist. With decreasing TiO_2/PVA ratio from 95/5 to 20/80 in the starting mixture of TiO_2 and PVA, n -value for the resultant Magneli phases tends to decrease from 9 to 2.

BET surface area of the samples is listed in Table 1 and SEM image is shown for some samples in Fig. 2.

The as-received rutile-phase TiO_2 (TP100) consists of nano-sized particles, as shown in Fig. 2a and has BET surface area of about $40 \text{ m}^2/\text{g}$. By the heat treatment up to 700°C (TP100-700), it shows sintering and growth of particles up to few micron-size, as shown in Fig. 2b, and BET surface area decreases to negligibly small. By the heat treatment together with PVA, on the other hand,

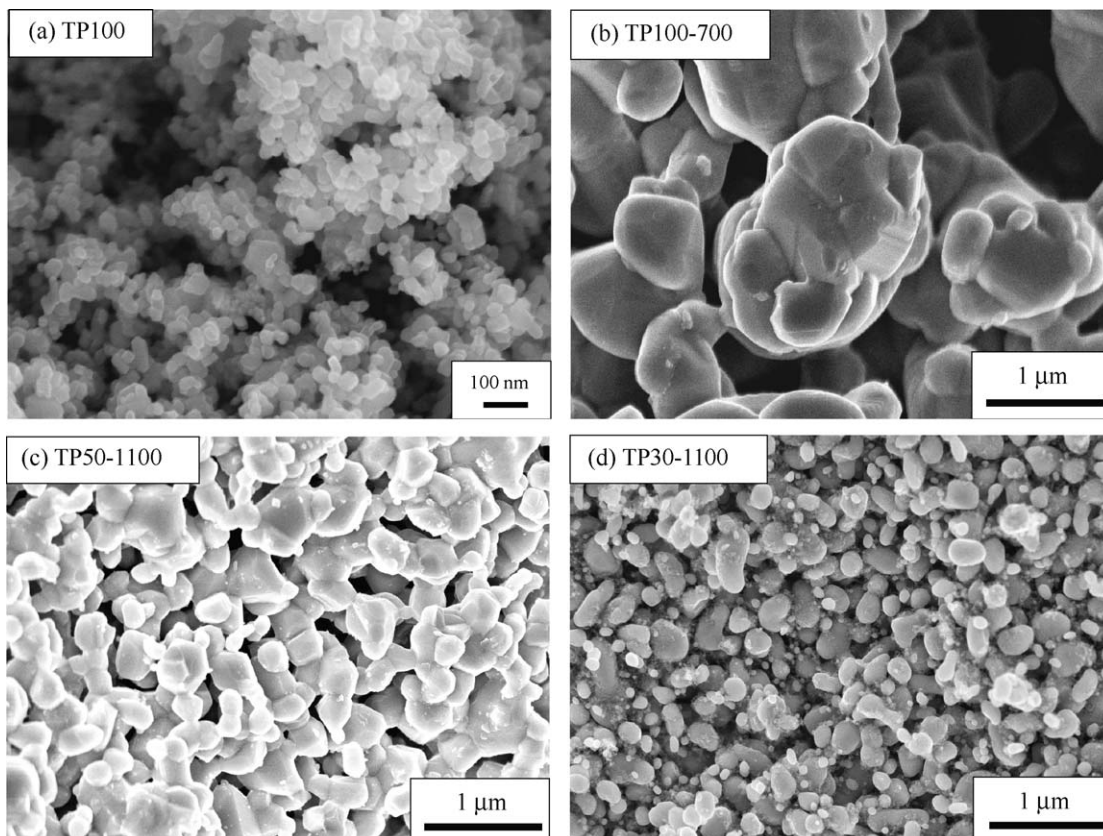


Fig. 2. Scanning electron micrographs of the sample: (a) TP100; (b) TP100-700; (c) TP50-1100; (d) TP30-1100.

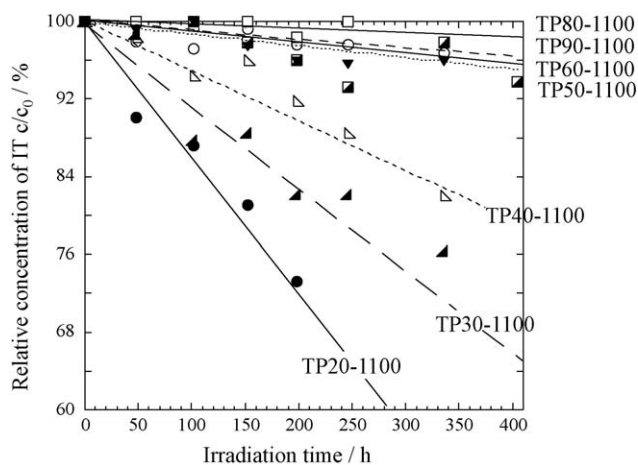


Fig. 3. Changes in relative concentration of iminoctadine triacetate (IT) remained in the solution c/c_0 with irradiation time t of visible light for carbon-coated $\text{Ti}_n\text{O}_{2n-1}$ samples prepared at 1100 °C.

sintering of TiO_2 grains is suppressed, more markedly with decreasing TiO_2 /PVA ratio, as shown for samples TP50-1100 and TP30-1100 in Fig. 2c and d, respectively. BET surface area increases rapidly with decreasing TiO_2 /PVA ratio up to 45 m^2/g , even though they are heat-treated up to a high temperature as 1100 °C.

3.2. Photocatalytic activity of carbon-coated $\text{Ti}_n\text{O}_{2n-1}$

In Fig. 3, relative concentration of IT remained in the solution c/c_0 in logarithmic scale is plotted against irradiation time of visible light, t , for the carbon-coated $\text{Ti}_n\text{O}_{2n-1}$ samples prepared at 1100 °C. The relation of $\ln(c/c_0)$ vs. t can be approximated to be linear, though there is some scattering of experimental points. From these linear relations, rate constant k for IT decomposition is calculated for each sample and shown in Table 1.

The samples TP40-1100, TP30-1100 and TP20-1100, in which main crystalline components are Ti_2O_3 and Ti_3O_5 , decompose IT molecules relatively quickly in comparison with other samples TP50-1100 and TP60-1100, in which main components are Ti_4O_7 . Among these three samples, sample TP20-1100 has a little higher k than sample TP40-1100, though the relative content of two $\text{Ti}_n\text{O}_{2n-1}$ phases, which is estimated from XRD patterns, is very similar with each other. This difference in k is reasonably supposed to be due to that in carbon content; TP20-1100 has a larger amount of carbon than TP40-1100, so that local concentration of IT around $\text{Ti}_n\text{O}_{2n-1}$ particle is expected to be higher in the former than in the latter. Since sample TP50-1100 is almost single phase of Ti_4O_7 and other three samples TP40-1100, TP30-1100 and TP20-1100 consist of Ti_2O_3 and Ti_3O_5 , the $\text{Ti}_n\text{O}_{2n-1}$ phases with n -value less than 3 are supposed to have higher photocatalytic activity under visible light than those with n -value of more than 4.

In Fig. 4, relative concentration of Ph remained in the solution c/c_0 in logarithmic scale is plotted against irradiation time of visible light t for some carbon-coated $\text{Ti}_n\text{O}_{2n-1}$ samples. From these linear relations, rate constant k for Ph decomposition is calculated for each sample and listed in Table 1.

Sample TP20-1100 has higher activity than TP50-1100 and TP80-1100. The relative photocatalytic activity for Ph decomposition among carbon-coated $\text{Ti}_n\text{O}_{2n-1}$ samples seems to be the same as that for IT under visible light.

In Figs. 3 and 4, the experimental points for each sample shows scattering, which is supposed to be caused from inhomogeneous distribution of different crystalline components with different n -values.

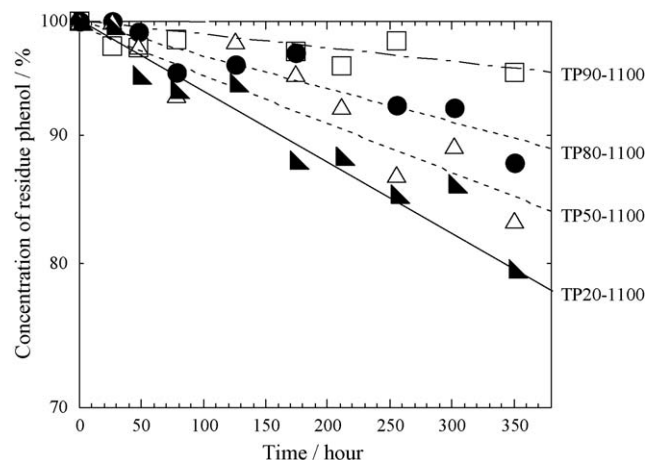


Fig. 4. Changes in relative concentration of phenol remained in the solution c/c_0 with irradiation time t of visible light for carbon-coated $\text{Ti}_n\text{O}_{2n-1}$ samples.

4. Discussion

During carbon coating, the matrix anatase-type TiO_2 was found to react with coated carbon to form Magneli phases, but the reaction was limited to be partially, probably just on the surface of TiO_2 particles [6,14,15]. However, the reaction was found to complete at a high temperature as 1100 °C by using rutile-type TiO_2 , as shown in Fig. 1. Magneli phases $\text{Ti}_n\text{O}_{2n-1}$ had been synthesized through the reduction of TiO_2 under ultrahigh vacuum and known to have a structure of oxygen vacancies, of which amount depended on n -value, into rutile framework in ordered manner [30,31]. In the present work, they can be synthesized by a simple process, i.e., heat treatment of the mixture with PVA at 1100 °C in inert atmosphere, although a possibility for remaining of a small amount of carbon cannot be avoided. However, the remained carbon in $\text{Ti}_n\text{O}_{2n-1}$ powder does not disturb their photocatalytic performance, even giving certain advantage, as shown in the present work.

On carbon-coated anatase-type TiO_2 , it was known that coated carbon layer strongly suppresses the sintering and consequent grain growth of TiO_2 [10,11]. The same effect of carbon layer was observed in the present case. Since carbon residues from the carbonization of PVA was not large amount in the samples from TP95-1100 to TP80-1100, the disturbance of sintering by carbon was not perfect, certain grain growth being observed, even though much less than that in TP100-700 without carbon. In TP50-1100 to TP20-1100, however, sintering of TiO_2 particles almost completely suppressed, as shown on TP30-1100 in Fig. 2d. Suppression of sintering of TiO_2 particles to keep them small may also help complete transformation of TiO_2 to Magneli phases, $\text{Ti}_n\text{O}_{2n-1}$, as discussed above.

On the present samples of carbon-coated $\text{Ti}_n\text{O}_{2n-1}$, their carbon content could not be measured because the weight decrease due to burning off the coated carbon is possibly compensated partially by the weight increase due to oxidation of $\text{Ti}_n\text{O}_{2n-1}$ phases to TiO_2 . However, it is reasonably supposed that carbon content increases with decreasing TiO_2 /PVA ratio, i.e., with increasing PVA content in the starting powder mixture. Also carbon coated by the present heat treatment condition is known to be porous from our works on the preparation of carbon-coated anatase-type TiO_2 [11] and also from those on porous carbons through carbon-coated MgO [34–37]. Therefore, the increase in apparent BET surface area for the samples of TP-50-1100 to TP20-1100 is reasonably supposed due to the carbon coated on minute $\text{Ti}_n\text{O}_{2n-1}$ particles.

Diffuse reflectance optical spectra of carbon-coated $\text{Ti}_n\text{O}_{2n-1}$ show absorption in whole range of wavelength from 250 to 700 nm, in contrast to a sharp decrease in absorbance above 400 nm for the original rutile-type TiO_2 (TP100). In the case of carbon-coated anatase-type TiO_2 , absorption for the light with wavelength above 400 nm was also observed, which was concluded to be due to the carbon coated. In the present carbon-coated $\text{Ti}_n\text{O}_{2n-1}$ samples also, carbon layer absorbs the light with whole range of wavelength measured and, as a consequence, any absorption edge was not observed in their diffuse reflectance spectra. Therefore, the band gap could not be estimated for the present carbon-coated $\text{Ti}_n\text{O}_{2n-1}$ phases.

In our previous paper [38], it was experimentally showed that commercially available Magneli phase sample, which consisted mainly of Ti_4O_7 with a small amount of Ti_5O_9 , absorbed the light in the whole wavelength range of 250–700 nm and showed certain photocatalytic activity for IT decomposition under visible light. Carbon coating on this powder was reported to give also certain enhancement of photocatalytic activity under visible light [38].

The present results on IT and Ph decomposition show that Magneli phases of $\text{Ti}_n\text{O}_{2n-1}$ are visible light sensitive photocatalysts, of which activity is governed by n -value, the phases with small n -values of 2 and 3 (Ti_2O_3 and Ti_3O_5) giving higher activity than those with other higher n -values. This result suggests that the presence of the higher concentration of oxygen vacancy is preferable for the higher activity under visible light; 1/4 of oxygen lattice sites is vacant in Ti_2O_3 , 1/6 in Ti_3O_5 , 1/8 in Ti_4O_7 and so on.

Carbon coating was shown to enhance photoactivity of anatase-type TiO_2 by improving its crystallinity and also increasing local concentration of pollutants around their particles [8–11]. Among the present samples, it was difficult to detect any difference in crystallinity of $\text{Ti}_n\text{O}_{2n-1}$, mainly because of a high heat treatment temperature as 1100 °C. Adsorption of IT and Ph was confirmed on carbon layer coated on TiO_2 particles [11]. On the present carbon-coated $\text{Ti}_n\text{O}_{2n-1}$ samples, adsorption of certain amount of IT and Ph was observed during keeping the sample powder dispersing in their aqueous solutions for 200 h in the dark, though quantitative determination of adsorptivity was not performed.

In our previous papers [6,13], carbon-coated anatase-type TiO_2 was proved to be fixed by using organic binder because it can be a barrier for direct contact between TiO_2 and binder and to be used repeatedly without marked reduction in photoactivity. The present carbon-coated $\text{Ti}_n\text{O}_{2n-1}$ phases are reasonably supposed to use repeatedly.

5. Conclusion

Carbon-coated Magneli phases $\text{Ti}_n\text{O}_{2n-1}$ with different n -values were prepared by a simple process, i.e., heat treatment of the powder mixture of rutile-type TiO_2 with carbon precursor PVA at 1100 °C in inert atmosphere. The n -value in $\text{Ti}_n\text{O}_{2n-1}$ phase could be controlled by changing TiO_2 /PVA ratio in the starting mixture, though most samples prepared in the present work are the mixed phases with different n -values. For exact control of n -value, more detailed studies on heat treatment conditions, particularly on mixing ratio of TiO_2 with PVA, are required.

Visible light activity was confirmed on these $\text{Ti}_n\text{O}_{2n-1}$ phase coated by carbon through the measurements of the decomposition

of IT and Ph in aqueous solution. Activity was supposed to depend strongly on n -value; low n -values as 2 and 3 gives higher activity than high n -values as 4–9.

Carbon coating gave various advantages; during heat treatment for carbon coating, simultaneous reduction of rutile-type TiO_2 to $\text{Ti}_n\text{O}_{2n-1}$ and suppression of sintering and grain growth of $\text{Ti}_n\text{O}_{2n-1}$ phases at high temperatures, and during decomposition of pollutants under visible light irradiation, enhancement of photocatalytic activity by concentrating the pollutant around photocatalyst particles.

References

- [1] M. Fujihira, Y. Satoh, T. Osa, *Nature* 293 (1981) 206–208.
- [2] D.F. Ollis, H. Al-Ekabi (Eds.), *Photocatalytic Purification and Treatment of Water and Air*, Elsevier, Amsterdam, 1993.
- [3] M.A. Fox, M.T. Dulay, *Chem. Rev.* 93 (1993) 341–357.
- [4] P. Pichat, *Catal. Today* 19 (1994) 313–334.
- [5] G. Riegel, J.R. Bolton, *J. Phys. Chem.* 99 (1995) 4215–4224.
- [6] T. Tsumura, N. Kojitani, I. Izumi, N. Iwashita, M. Toyoda, M. Inagaki, *J. Mater. Chem.* 12 (2002) 1391–1396.
- [7] M. Inagaki, Y. Hirose, T. Matsunaga, T. Tsumura, M. Toyoda, *Carbon* 41 (2003) 2619–2624.
- [8] B. Tryba, T. Tsumura, M. Janus, A.W. Morawski, M. Inagaki, *Appl. Catal. B: Environ.* 50 (2004) 177–183.
- [9] B. Tryba, A.W. Morawski, T. Tsumura, M. Toyoda, M. Inagaki, *J. Photochem. Photobiol. A: Chem.* 167 (2004) 127–135.
- [10] M. Inagaki, F. Kojin, B. Tryba, M. Toyoda, *Carbon* 43 (2005) 1652–1659.
- [11] M. Toyoda, B. Tryba, F. Kojin, S. Mozia, T. Tsumura, E. Itoh, M. Inagaki, *TANSO* 2005, No. 220, 2005, 289–299.
- [12] M. Toyoda, B. Tryba, F. Kojin, T. Tsumura, M. Inagaki, *Adsorpt. Sci. Technol.* 46 (2006) 180–187.
- [13] M. Inagaki, M. Nonaka, F. Kojin, T. Tsumura, M. Toyoda, *Environ. Technol.* 27 (2006) 521–528.
- [14] T. Tsumura, Y. Hattori, K. Kaneko, M. Inagaki, M. Toyoda, *Desalination* 169 (2004) 269–275.
- [15] M. Toyoda, T. Yano, T. Tsumura, Y. Amao, M. Inagaki, *J. Adv. Oxid. Technol.* 9 (2006) 49–52.
- [16] H. Irie, Y. Watanabe, K. Hashimoto, *Chem. Lett.* 32 (2003) 772–773.
- [17] Y. Choi, T. Umehayashi, M. Yoshikawa, *J. Mater. Sci.* 39 (2004) 1837–1839.
- [18] M. Shen, Z. Wu, H. Huang, Y. Du, Z. Zou, P. Yang, *Mater. Lett.* 60 (2006) 693–697.
- [19] T. Ohno, T. Tsubota, K. Nishijima, Z. Miyamoto, *Chem. Lett.* 33 (2004) 750–751.
- [20] M. Janus, B. Tryba, M. Inagaki, A.W. Morawski, *Appl. Catal. B: Environ.* 52 (2004) 61–67.
- [21] M. Janus, M. Inagaki, B. Tryba, M. Toyoda, A.W. Morawski, *Appl. Catal. B: Environ.* 63 (2006) 272–276.
- [22] T. Umehayashi, T. Yamaki, H. Itoh, K. Asahi, *Appl. Phys. Lett.* 81 (2002) 454–456.
- [23] T. Ohno, M. Akiyoshi, T. Umehayashi, K. Asai, T. Mitsui, M. Matsumura, *Appl. Catal. A: Gen.* 265 (2004) 115–121.
- [24] R. Asahi, T. Morikawa, T. Ohwaki, K. Aoki, Y. Taga, *Science* 293 (2001) 269–271.
- [25] T. Lindgren, J.M. Mwabora, E. Avendano, J. Jonssoon, A. Hoel, C.G. Granqvist, S.E. Lindquist, *J. Phys. Chem. B* 107 (2003) 5709–5716.
- [26] J.L. Gole, J.D. Stout, C. Burda, Y. Lou, X. Chen, *J. Phys. Chem. B* 108 (2004) 1230–1240.
- [27] H. Tokudome, M. Miyauchi, *Chem. Lett.* 33 (2004) 1108–1109.
- [28] M. Anpo, Y. Ichihashi, M. Takeuchi, M. Yamashita, *Rev. Chem. Intermed.* 24 (1998) 143–149.
- [29] T. Ohno, T. Tsubota, M. Toyofuku, R. Inaba, *Catal. Lett.* 98 (2004) 255–258.
- [30] L.A. Bursill, B.G. Hyde, *Prog. Solid State Chem.* 7 (1972) 177–253.
- [31] H. Noerenberg, G.A.D. Briggs, *Surf. Sci.* 402–404 (1988) 738–741.
- [32] F. Kojin, M. Mori, T. Morishita, M. Inagaki, *Chem. Lett.* 35 (2006) 388–389.
- [33] F. Kojin, M. Mori, Y. Noda, M. Inagaki, *Appl. Catal. B: Environ.* 78 (2008) 202–209.
- [34] M. Inagaki, S. Kobayashi, F. Kojin, N. Tanaka, T. Morishita, B. Tryba, *Carbon* 42 (2004) 3153–3158.
- [35] T. Morishita, R. Suzuki, T. Nishikawa, T. Tsumura, M. Inagaki, *TANSO* 2005, 2005, pp. 226–231 (in Japanese).
- [36] T. Morishita, Y. Soneda, T. Tsumura, M. Inagaki, *Carbon* 44 (2006) 2360–2367.
- [37] T. Morishita, R. Suzuki, T. Tsumura, H. Habazaki, M. Inagaki, *TANSO* 2006, 2006, pp. 220–226 (in Japanese).
- [38] M. Toyoda, T. Yano, S. Mozia, T. Tsumura, E. Itoh, Y. Amao, M. Inagaki, *TANSO* 2005, 2005, pp. 265–269 (in Japanese).